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THE ROLE OF ALKALIS AND CONSERVING RESOURCES IN BLAST-FURNACE SMELTING

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In ferrous metallurgy, the potential for conserving resources is often determined by the behavior of the impurity elements in metals production. This behavior may be highly complex, and its features may be interpreted differently by different experts. For example, the presence of zinc and alkali metals in the blast-furnace charge is known to result in excessive coke consumption, a reduction in the productivity of the furnace, an increase in the yield of top dust, shortening of the campaign, and in some cases to complete destabilization of the smelting operation. In choosing a technology for blast-furnace smelting, accounting for the entry of alkali metals and zinc into the furnace is one of the most important factors that determines the expediency of controlling the heat "from the top" or "from the bottom," features of the slag formation process, the gasdynamics of the smelting operation, and other characteristics.

The special importance of alkali metals and their compounds to the running of a blast furnace has long been known. Nearly 200 years ago, in his work "Traitte de Chemia" (in the section on iron) the eminent chemist I. J. Bercellius was describing the chemical transformations that iron undergoes in metallurgical production. In so doing, he was perhaps the first to have mentioned the remarkable materials that are formed in a blast furnace and that can be seen after the furnace has been blown out. Among these materials in particular are common salt (NaCL), potassium chloride (KCl), and potassium cyanide (KCN).

Since that time, the behavior of alkali metals in blast-furnace smelting has been the subject of continuous research throughout the world. The largest study of this subject in our country was the study done (1931–1932) on the smelting of titanium-magnetite ores in blast furnaces at the Verkhne-Turinsk and Nizhniy Tagil plants with the use of coke obtained from a charge containing additions of common salt (this so-called "salt" coke contained about 5% NaCL). During the heats, from 120 to 250 kg of NaCl entered the furnace for each ton of pig iron smelted. With the slag having had a basicity $(CaO + MgO)/(SiO_2 + Al_2O_3) = 0.8$ and an Na_2O content of 2.8%, furnace operators could not remove more than 50 kg of sodium from the furnace. Most of it was removed through the top along with the top gases. The rest of the sodium accumulated in the furnace, rapidly destroying the lining. Nevertheless, after two trial periods of furnace operation lasting 15 and 10 days, the factories were able to smelt about 2500 tons of vanadium pig iron.

M. A. Pavlov was heavily involved in the study of the behavior of alkalis in blast furnaces. In his research conducted during the 1940s, he became probably the first scientist in this country to examine the mechanism of circulation and accumulation of alkali metals during the reactions that form their cyanides and carbonates:

$$K_2CO_3 + 4C + N_2 \leftrightarrow 2KCN + 3CO,$$

$$Na_2CO_3 + 4C + N_2 \leftrightarrow 2NaCN + 3CO.$$

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TABLE 1. Allowable Alkali Load on the Blast Furnaces of Companies in Several Western Nations

Nation	Company	Allowable alkali load, kg/ton pig
Canada	STIKLO Dofasko	3.0
Japan	Kawasaki Seitetsu, Kobe Seikose, Sin Nippon Seitetsu, Nippon Kokan	2.5–3.1
U.S.	Ellenwood Steel, Jones and Laughlin Steel, United States Steel	3.2–4.5
England	British Steel	3.5
Germany	August Thyssen-Hütte	4.0
Switzerland	Grenges	5.5

The same problem also occupied an important place in the studies conducted on idled blast furnaces under the guidance of I. D. Balon. It was a coincidence that both researchers worked with very high yields of alkalis – 19.4 kg/ton pig. No more than 4.5 kg/ton pig could be removed with the slag. The studies led to important conclusions in regard to the participation of alkalis in the formation of the primary slags in blast-furnace smelting and the effects of alkalis on the breakdown of the charge materials and the structure and boundaries of the loop about which alkali metals circulate in the furnace.

Research into the effect of alkalis on blast-furnace smelting peaked during the 1970s. This period was characterized first of all by the construction of powerful blast furnaces and a strong trend toward the use of large quantities of iron-ore pellets in the charge. In certain countries, especially Canada, blast furnaces were built to operate on a charge in which the iron-ore-based portion was comprised of 80–100% pellets. At the same time, problems related to the activity of alkalis during smelting became so acute that a special commission was organized by the "Ernkontorens" Metallurgical Society in Switzerland in 1972 to study this problem.

Smelting in blast furnaces is adversely affected by K and Na in the following manner. Compounds of alkali metals deposited on the surface of the coke act as a catalyst and intensify the gasification of carbon in the presence of CO_2. The gasification reaction is shifted toward lower temperatures and is accompanied by a reduction in the strength of the coke.

Coke strength is reduced most by potassium: in addition to speeding up the gasification reaction, potassium present in the pores and cracks of the coke leads to the formation of compounds of the type $K_2O \cdot SiO_2$ and $K_2O \cdot Al_2O_3 \cdot 2SiO_2$. This is accompanied by an increase in the volume of the coke and its subsequent fracture.

The condensation of compounds of alkali metals on the surface of the lining of furnaces is one reason for incrustation of the bottom part of the stack and the bosh. High (30%) total concentrations of potassium and sodium have been observed, for example, in the crusts formed in blast furnaces at the Magnitogorsk and Chelyabinsk metallurgical combines.

The action of potassium compounds is the main reason for the destruction of the refractory lining of blast furnaces in the lower part of the stack, the bosh, and in some cases the tuyere zone of the hearth. In these regions, potassium actively penetrates the monolithic alumosilicate lining. This leads to the formation of new minerals (such as the silicide $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ or leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$) and rearrangement of the crystalline lattice of the refractories, which is accompanied by a reduction in their softening point and mechanical strength. In carbon refractories, potassium atoms can penetrate the crystalline lattice of the carbon. This creates stresses that causes cracks to form. In the tuyere zone, the situation is aggravated by the formation of an aggressive condensed phase based on KCN.

Condensation of compounds of alkali metals on the surface of sinter and pellets leads to their fracture and a deterioration in the gas permeability of the stock. Pellet disintegration occurs particularly rapidly under the influence of alkalis. The

TABLE 2. Sodium and Potassium Balance in Blast Furnaces, g/ton pig

Balance item	"Severstal'" Company		NLMK		AK "Tulachermet"	
	N	K	N	K	N	K
Input						
iron-ore part	335	2230	500	1370	750	6750
coke	45	145	180	430	150	500
Total	380	2375	680	1800	900	7250
Output:						
to pig iron	20	12	8	20	2	10
to slag	350	1625	660	1295	873	5850
to sludge	5	15	3	15	10	15
Difference*	5(1.3%)	723(30.1%)	9(1.3%)	470(26.0%)	15(1.6%)	1375(18.9%)

*Sodium and potassium that remain in the furnace, enter the lining, or are not removed during gas-cleaning.

presence of alkali metals also adversely affects the viscosity of basic blast-furnace slags, which promotes the formation of alkaline alumosilicate groups (such as $K_2O{\cdot}Al_2O_3{\cdot}2SiO_2$) in the slag melt.

Reacting with oxides of iron, compounds of potassium and sodium that leave the furnace with the top gases help form iron-bearing slags in the hot-blast line and in the passageways of the checkerwork of the stoves.

The full effect of alkalis on the indices of blast-furnace smelting was most thoroughly studied and generalized in investigations conducted by specialists of the firm STIKLO (Canada) and in the research done by S. Heransson (Switzerland). According to these sources, the productivity of large blast furnaces – which are the blast furnaces most sensitive to changes in the gas permeability of the stock – is reduced by 3–8% and coke consumption is increased by the same amount when the content of alkalis in the charge increases by 1 kg/ton pig iron. The main methods that can be used to reduce the content of alkalis in blast furnaces are as follows:

- reducing the content of alkalis in the charge materials;
- removing top dust and blast-furnace slag (which have high concentrations of alkalis) from the sintering-machine charge;
- operating the furnace on acid slags;
- increasing the volume of slag, especially in furnaces in which slag volume is already low (with a significant percentage of pellets in the charge).

Most companies in the leading industrial nations have established a limiting alkali load for blast furnaces, i.e., have set limits on the amounts of potassium and sodium (in oxide form) that can be present in the charge materials without changing the smelting practice (Table 1).

Before these limits were set, the amount of alkalis (in oxide form) that entered the blast furnaces at these companies was 8–14 kg/ton pig.

Alkalis enter a blast furnace with the charge materials. Here, the main sources of alkalis are not usually iron ores or their concentrates, but instead the fluxes and strengthening additions used in making the pellets for the blast-furnace charge. For example, the iron-ore concentrates at the Lebedinsk, Stoilensk, Olenegorsk, Kovdorsk, and Kostamuksha mining-metallurgical combines contain 0.08–0.12% alkali oxides, while limestones contain 0.2–0.6%. The content of alkali oxides in the concentrate may reach 0.5% only in certain cases (such as under the conditions which exist at the Mikhailovsk Mining-Concentration Combine). The content of alkali metals in the coke depends on many factors and fluctuates from 0.04 to 0.25%.

During the period 1996–1998, the Department of Ore-Roasting Processes at the Moscow State Institute of Steel and Alloys worked with specialists at Giredmet (State Scientific Research and Planning Institute of the Rare Metals Industry) on studies of the behavior of alkali metals in blast furnaces in the European part of Russia. The alkali load on the furnaces was determined to be as follows: 3.2–3.4 kg/ton pig at OAO "Severstal'"; 3.05–3.3 kg/ton pig at the Novolipetsk Metallurgical Combine (NLMK); 7.8 kg/ton pig at AK "Tulachermet".

TABLE 3. Lithium and Rubidium Balance in Blast Furnaces, g/ton pig

Balance item	AO "Severstal'"		NLMK		AK "Tulachermet"	
	Li	Rb	Li	Rb	Li	Rb
Input						
iron-ore part	60	30	15	40	13	13
coke	18	Traces	20	42	8	21
Total	78	30	35	82	21	34
Output:						
to pig iron	8	1	Traces	Traces	Traces	not detected
to slag	55	24	25	30	14	9
to sludge	1	Traces	Traces	Traces	Traces	Traces
Difference	14(18.0%)	5(16.6%)	10(28.6%)	52(64.6%)	7(33.3%)	23(67.0%)

TABLE 4. Chlorine and Fluorine Balance in Blast Furnaces, g/ton pig

Balance item	AO "Severstal'"		NLMK		AK "Tulachermet"	
	Cl	F	Cl	F	Cl	F
Input						
iron-ore part	64	206	66	210	123	31
coke	43	9	9	7	6	13
Total	107	215	75	217	129	44
Output:						
to pig iron	10	Traces	5	Traces	8	Traces
to slag	3	108	25	102	5	13
to sludge	1	2	Traces	1	1	1
to gas phase	93	105	45	114	115	30

The alkali metals balance for these furnaces is shown in Table 2.

An analysis of the results shows the following: sodium and potassium enter the pig iron in every case (albeit in small amounts), which must be taken into account in the production of high-quality pig irons in which the concentrations of micro-impurity elements is generally limited to 20–30 g/ton pig; potassium has a greater effect on smelting indices, since sodium is almost completely (94–98%) removed from the furnace in the slag. The difference in the potassium balance, due to its accumulation in the circulation cycle, penetration into the lining, etc., is 20–30% (rel.).

The characteristic features of the behavior of sodium and potassium are seen whether the quantities of alkali metals that enter the blast furnace are small ("Severstal'" and NLMK) or large ("Tulachermet").

We also studied the behavior of other alkali metals in blast-furnace smelting – lithium and rubidium – and the halogens chlorine and fluorine, since they are often present with alkali metals in the minerals used in metallurgical operations. The resulting data (Tables 3 and 4) showed that the amounts of lithium and rubidium that may accumulate in the circulation cycle, build up in the furnace lining, or be carried out of the furnace through the top are comparable to sodium (which until now has received most of the attention from specialists); the differences in the chlorine and fluorine balances, which is due to the transfer of these elements to the gas phase, are also comparable in absolute value to the corresponding differences for the alkali metals. In light of the high chemical activity of alkali metals and halogens, it can be assumed that their reaction could have a significant effect on the behavior of alkali metals in blast furnaces. A circulation loop may be formed in the furnace for the halogens as well as the alkali metals.

In our opinion, the above facts require reconsideration of existing representations of the behavior of alkali metals in blast-furnace smelting. It is necessary to account for the complex nature of the reaction of these metals (including lithium and rubidium) with different phases in the smelting operation, including halogens.